The Development of a Novel Gold Alloy with 995 Fineness and Increased Hardness

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The mechanical properties and processing of a newly developed ternary Au-Sb-Co alloy with 995 fineness are discussed. The high gold content of this alloy (99.5 per cent) facilitates marking as 24 carat gold (or *Chuk Kam*) in many countries. The alloy has a rich yellow colour, virtually identical to that of pure gold, and can be hardened to a peak hardness of 130 to 140 points on the Vickers hardness scale using a combination of cold work and a low temperature (250 to 300°C) ageing heat treatment. This hardness is comparable to that of cold-worked 22 carat yellow gold, and almost double the maximum hardness that can be obtained in pure gold. The 995 alloy is highly formable, and is amenable to casting, granulation, remelting, wire drawing, forming and rolling.

The global demand for high-caratage gold jewellery appears to be on the increase, with more consumers preferring the high quality and rich colour of jewellery alloys with high gold contents (at least 75 weight per cent) (1). While the trend in the western world is moving towards higher quality jewellery, demand has remained strong in Asia, a region traditionally associated with a preference for high-caratage gold alloys.

Asian countries combined are the largest consumers of gold jewellery in the world (2). The high-caratage segment of the jewellery market in this region predominates, and a considerable demand exists for 24 carat gold jewellery in particular. In these markets gold has traditionally been purchased as an investment and as a hedge against political uncertainties (3). This attitude has changed in recent years, with more customers buying pure gold (such as *Chuk Kam*) jewellery with modern designs for adornment (4). Unfortunately, pure gold is generally considered too soft for jewellery purposes, having hardness values in the as-cast and cold-worked condition below 80 HV (points on the Vickers hardness scale).

This move away from purchasing pure gold jewellery for investment purposes, into a market for 24 carat jewellery as fashion accessories, creates a demand for a harder, more abrasion resistant 24 carat gold alloy, able to withstand the demands of everyday wear. The development of a gold alloy containing one per cent titanium (Gold 990) demonstrated that it is possible to improve the hardness and wear resistance of gold through the addition of small amounts of alloying elements (microalloying) (5). Unfortunately this alloy has enjoyed only limited success in the high-caratage jewellery market, since its production requires sophisticated melting and processing equipment. The presence of titanium also makes Gold 990 scrap more difficult to remelt and recycle (6). Its development, however, encouraged the authors to believe that it would be possible to develop a hard, wear resistant alloy with at least 995 fineness (a minimum gold content of 99.5 weight per cent) that could be processed with existing equipment and that would be amenable to remelting. The higher gold content of such an alloy, compared to that of Gold 990, would facilitate hallmarking (marking by an independent, accredited third party) or marking (by the manufacturer, retailer, importer, *etc*) as 24 carat gold or *Chuk Kam* in many of the countries where a demand exists for pure gold jewellery.

Actually, a number of these microalloyed gold alloys have been developed in recent years, as described in a recent review by Corti (6). These alloys generally rely on significant amounts of cold work, in combination with dispersion or precipitation hardening, to achieve the desired mechanical properties. Calcium appears to be the principal microalloying element, often used in combination with small amounts of other elements, most notably beryllium, gadolinium and/or other rare earth elements, to enhance the hardening effect. Unfortunately remelting, of these alloys is generally associated with significant reductions in strength due to alloying element losses, and many of the required alloying elements are rare, expensive and are not always easy to incorporate into the gold.

In order to address these problems, the authors developed a hard '24 carat' gold alloy that can be processed with existing equipment and which is amenable to remelting without any significant loss in strength. The alloy contains 99.5 per cent gold, has a colour virtually identical to that of pure gold and can be hardened to a hardness comparable to that of cold-worked 22 carat yellow gold. This is almost double the maximum hardness that can be obtained in pure gold. A patent has been filed (M. du Toit, S. African Patent 2000/7053, Mintek, Filed 30 November 2000).

Chemical Composition and Hardening Mechanism

The nominal composition of the 995 alloy is shown in Table 1. Antimony and cobalt were selected as hardening agents on the basis of the binary Au-Sb and Au-Co phase diagrams shown in Figures 1 and 2 (7).

Although the solubility of antimony in gold is limited (see Figure 1), the phase diagram predicts that up to approximately one per cent antimony can dissolve in gold at temperatures between about 500 and 700°C. Any decrease in temperature below approximately 500°C is associated with a reduction in solid solubility so that the solubility of antimony in gold is negligible at temperatures below approximately 300°C. This is characteristic of a potential precipitation hardening system. An initial investigation (8) showed that a binary Au-Sb alloy containing 99.5 per cent gold and 0.5 per cent antimony work-hardens at a very rapid rate, resulting in a high hardness after deformation. Unfortunately, the recrystallisation temperature of this alloy appears to be very low and ageing at 250°C after deformation to induce precipitation hardening results in a rapid decline in hardness to a value below that required by the jewellery industry.

The binary Au-Co phase diagram shown in Figure 2 also displays precipitation hardening potential. The solubility of cobalt in gold decreases from a maximum of 8 per cent at the eutectic temperature to virtually zero at temperatures below approximately 500°C. A binary Au-Co alloy (99.5 per cent gold and 0.5 per cent cobalt) work-hardens at a much slower rate than the corresponding binary Au-Sb alloy, but the hardness of

Table 1 *The Nominal Composition of the New 995 Alloy (Percentage by Mass)*

Au	Sb	Co
99.5	0.3	0.2

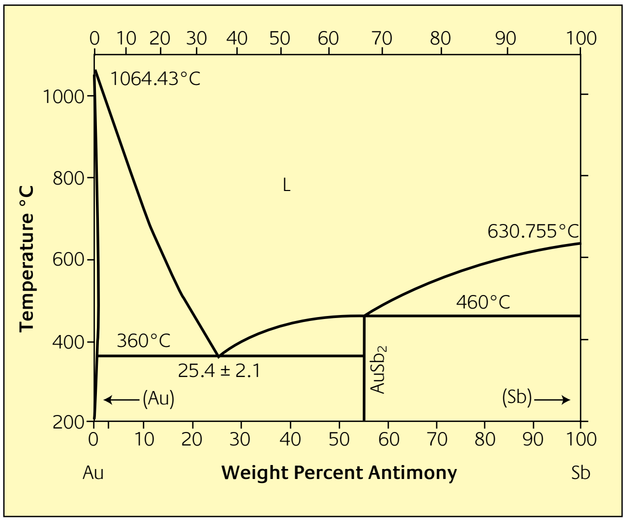

Figure 1
The binary Au-Sb phase diagram (7). (Reprinted with permission from ASM International)

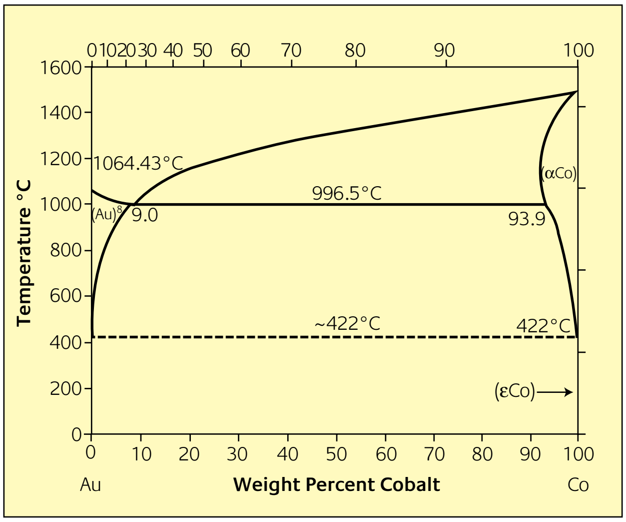

Figure 2
The binary Au-Co phase diagram (7). (Reprinted with permission from ASM International)

a deformed sample does not decrease during subsequent ageing at 300°C (8). This suggests that the presence of cobalt retards recrystallisation in gold. Similar results have been reported by Raub and Ott (9) for 14 and 18 carat gold alloys.

In an attempt to combine the benefits of possible precipitation hardening, rapid work-hardening and retarded recrystallisation, the ternary Au-Sb-Co system was investigated. The combination of antimony and cobalt in gold proved to be very successful, with an alloy containing 0.3 per cent antimony and 0.2 per cent cobalt in gold showing the greatest hardening potential (8).

Transmission electron microscope (TEM) studies confirmed that a low temperature ageing heat treatment after solution annealing and quenching induces the

Table 2 *Requirements for 24 Carat Gold in the Far East and Asia (According to the Regional World Gold Council Offices)*

Country	Minimum Gold Content Requirement	Can the Mintek 995 Alloy Meet the Requirement?
China	**99.0%** can be marked as *Chuk Kam*	Yes
Taiwan	**99.5%** can be marked as 24 carat	Yes
Hong Kong	**99.0%** can be marked as *Chuk Kam*	Yes
Japan	**99.85%** can be marked as 24 carat	No
South Korea	**99.4%** can be marked as 24 carat	Yes

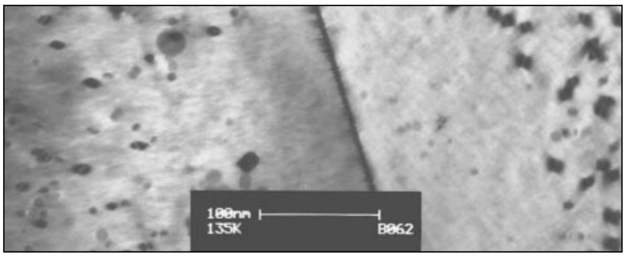

Figure 3
TEM micrograph of an overaged sample of the 995 alloy showing small disc-shaped Sb-rich precipitates in the gold matrix

precipitation of small (less than 20 nm in diameter) antimony-rich particles in the matrix of the new 995 alloy. These particles appear to be disc-shaped and are generally uniformly distributed within the gold grains. Figure 3 is a TEM micrograph showing these precipitates after a heat treatment at 300°C for 50 hours to overage or coarsen the particles. The hardening mechanism of the alloy will be considered in more detail in a separate publication.

The high gold content of the alloy (99.5 per cent) facilitates marking as 24 carat gold in many countries, including South Africa and much of Europe. Legal standards for 24 carat gold in Asia are more stringent (see Table 2), but the new alloy can be marked as 24 carat gold in Taiwan and Korea, and as *Chuk Kam* in China and Hong Kong. These four countries are amongst the biggest consumers of 24 carat gold or *Chuk Kam* jewellery in the global market.

Some of the properties of the new alloy have already been described in an earlier publication (10). The remainder of this paper will focus on the mechanical properties of the 995 alloy and its performance during laboratory testing and industrial scale trials.

The Hardness and Heat Treatment of the 995 Alloy

A comparison between the hardness of the hard 995 alloy, pure gold (4N according to DIN 8238), and 22 carat yellow gold (91.7Au-5.5Ag-2.8Cu) in three conditions is shown in Table 3. (All hardness measurements quoted were performed on the sample surface with an applied load of 5 kg). The figures in italics refer to the maximum hardness that can be achieved in each of these materials. It is evident that the peak hardness that can be obtained in the 995 alloy is comparable to that of 22 carat gold in the cold-worked condition, and almost double that of heavily cold-worked pure gold. The hardness of the alloy compares favourably with the published hardness values of other microalloyed 24 carat alloys (6).

The 995 alloy is hardened using a combination of cold work (deformation) and a low-temperature ageing heat treatment

Table 3 *The Hardness of Pure Gold, 22 Carat Yellow Gold and the New 995 Alloy in a Number of Different Conditions (HV5:Points on the Vickers Hardness Scale; Applied Load of 5 kg)*

Material	Annealed	Cold-worked	Aged
995 alloy	32 HV5	100 HV5 (70% reduction in thickness)	Peak hardness: ***142 HV5*** (hardened at 250°C) Peak hardness: ***131 HV5*** (hardened at 300°C)
Pure gold	22 HV5	***73 HV5*** (70% reduction in thickness)	Cannot be hardened by heat treatment to any appreciable extent
22 carat gold (11)	52 HV5	***138 HV5*** (75% reduction in thickness)	Cannot be hardened by heat treatment to any appreciable extent

that induces the precipitation hardening reaction. In order to obtain peak hardness, a three step procedure is recommended:

1 ***Solution Annealing:*** The alloy is annealed at temperatures between 650 and 750°C for up to one hour (depending on the component dimensions) to dissolve the alloying elements in the gold matrix, followed by rapid quenching in water to retain the elements in metastable solution down to room temperature. Should the grain size of the final product be of importance, for example in coining applications, the alloy can be cold worked prior to the annealing stage. Accurate control of the solution annealing temperature is essential to prevent selective melting and liquation of the grain boundaries, and annealing temperatures towards the lower end of the specified range are recommended. Any tarnish layer formed during the annealing heat treatment can be removed by mechanically buffing the surface of the article, or by immersing the component in *aqua regia* for a few seconds. In order to prevent the formation of a tarnish layer during the annealing cycle, commercially available salt, such as Degussa GS 430, can be used as a flux.

2 ***Deformation:*** After annealing and quenching, the alloy can be cold worked or deformed. The alloy work-hardens rapidly under deformation, resulting in much higher hardness values in the deformed condition than those of pure gold (refer to Figure 4). Because cold work results in an appreciable hardness increase in the alloy, at least 20 per cent reduction is recommended. The alloy is very formable in the annealed condition, and high reductions can be tolerated.

3 ***Ageing:*** An additional increase in hardness can be obtained by ageing the cold-worked material at a temperature between 250 and 300°C to induce precipitation of the antimony-rich precipitates described earlier. Although the peak hardness that can be achieved is higher after ageing at a temperature of 250°C (142 HV5), the hardening process is significantly slower and the maximum hardness is only reached after an extended time at temperature. As shown in Figure 5, the time required to reach the peak hardness (131 HV5) at 300°C is reduced to only about 3½ hours. The peak hardness also depends on the amount of deformation prior to ageing. Although the alloy displays significant hardening in the annealed condition (no deformation prior to ageing), the peak hardness during ageing at 300°C (97 HV5) is much lower than the peak hardness of material that was deformed 25 per cent (118 HV5) and 70 per cent (131 HV5), respectively, prior to ageing.

The higher hardness of the 995 alloy, compared to that of pure gold, eases machining and polishing, and facilitates the production of jewellery pieces with more complicated designs and intricate shapes. Greater wear resistance and reduced susceptibility to scratching and damage are also envisaged.

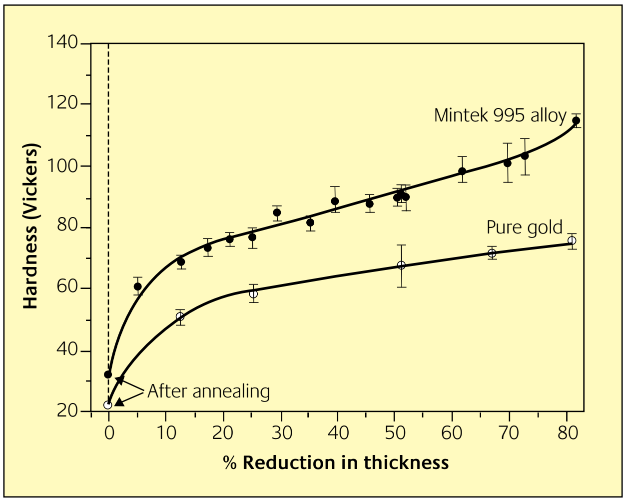

Figure 4
The change in hardness of the new 995 gold alloy and pure gold as a function of the percentage reduction in thickness during rolling (with 95% confidence interval)

Mechanical Properties

The tensile properties of the new 995 alloy were measured using flat tensile samples with gauge lengths of 25mm. The results are shown in Table 4, and in Figures 6 and 7 as a function of the amount of prior deformation in the annealed, cold-worked, and cold-worked and aged conditions. It is evident that a combination of deformation and ageing provides optimum strengthening in the alloy. The results also confirm that a higher level of deformation prior to ageing increases the strength of the alloy after heat treatment. The maximum tensile strength of the 995 alloy is about twice that of cold-worked pure gold (4N).

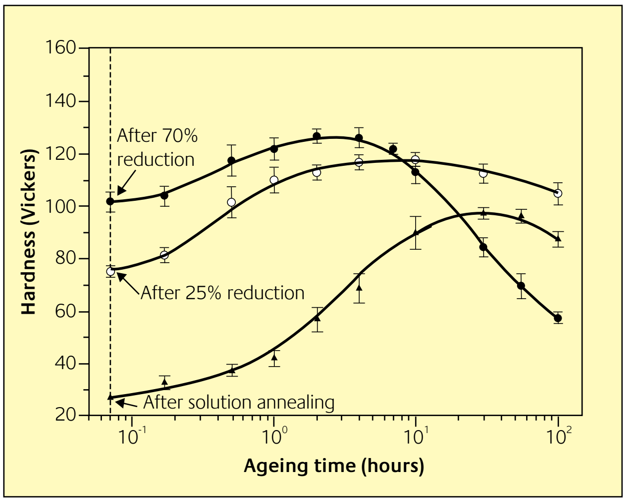

Figure 5
The change in hardness of the alloy during ageing at 300°C as a function of time and the amount of rolling reduction prior to ageing (with 95% confidence interval)

Table 4 *Mechanical Properties of the New 995 Alloy*

	Annealed	Cold-worked (20% Reduction in Thickness)	Cold-worked (80% Reduction in Thickness)	Cold-worked (80% Reduction in Thickness) and Aged
Ultimate tensile strength	160 MPa	220 MPa	330 Mpa	360 MPa
Yield strength (0.2% proof stress)	40 MPa	210 MPa	330 Mpa	340 MPa
Elongation to fracture	46 %	Not available	Not available	12 %

The formability of the 995 alloy in the annealed condition was evaluated using deep drawing/earing and Erichsen cupping tests. The deep drawing/earing test was performed on 1 mm thick sheet by drawing the material into a flat-bottomed cup. Thinning appeared to be uniform and the specimen did not fail during the test. No dramatic 'ears' or wavy edges formed on top of the drawn cup, demonstrating little or no planar anisotropy. Three Erichsen cupping tests were performed on 0.7mm thick sheet using a 23mm diameter ball as indentor or doming punch. A dome height of 11 mm was obtained before fracture, which indicates that the alloy has good formability, not withstanding its increased strength and rate of work-hardening.

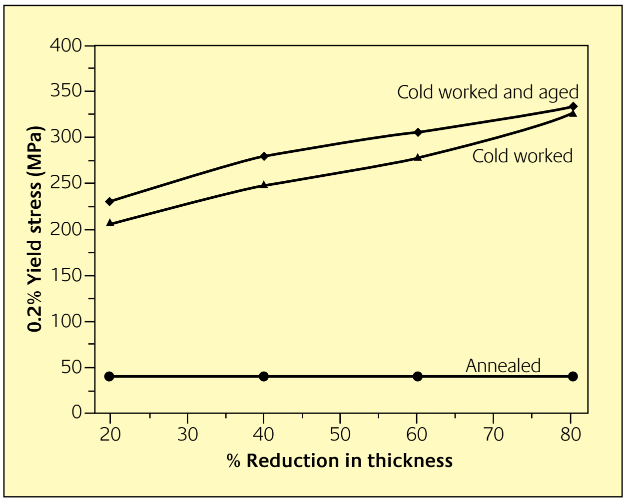

Figure 7
The influence of cold work, annealing and ageing on the 0.2 per cent yield stress of the new 995 alloy as a function of the amount of prior deformation

Castability

Although the alloy is more amenable to the production of wrought jewellery, successful casting trials have been carried out in jewellery workshops and on industrial scale.

Laboratory Scale Casting Trials

In order to evaluate the castability of the new 995 alloy, a series of investment casting trials was performed with the assistance of two manufacturing jewellers. During these trials, pure gold granules and the required alloying additions (also in pure granular form) were melted under a protective atmosphere (argon or nitrogen) using induction melting equipment, or in air using an oxyfuel flame with a suitable flux. The molten metal was cast into a preheated flask and allowed to solidify before being quenched in water. No surface film formed on the liquid metal, which remained very fluid during the entire casting operation. The hardness of the alloy was approximately 61 HV5 after investment casting, twice that of pure gold in the as-cast condition (approximately 30 HV5).

If the casting is quenched from a sufficiently high temperature after solidification, the alloying elements can be retained in solid solution without requiring solution annealing and subsequent softening. Subsequent ageing at 300°C results in an increase in hardness to approximately 87 HV5 after one hour at temperature (a hardening curve at 300°C after casting is shown in Figure 8). If the casting is not quenched and the cooling rate after solidification is slow, the alloying elements will not remain in solution, and very little hardening will take place on ageing, unless the casting is solution annealed prior to hardening. Solution annealing after

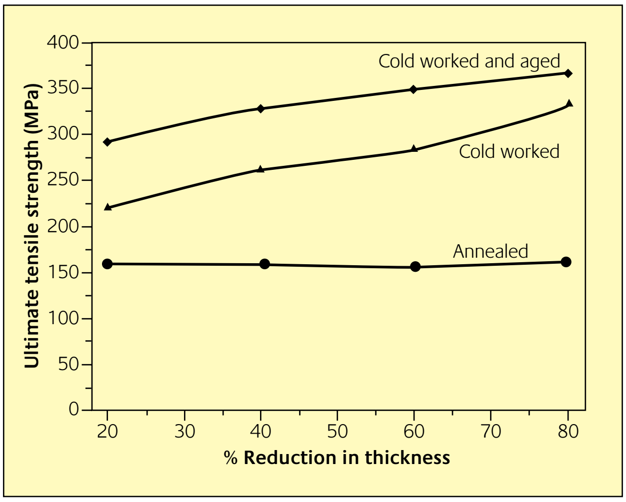

Figure 6
The influence of cold work, annealing and ageing on the ultimate tensile strength of the new 995 alloy as a function of the amount of prior deformation

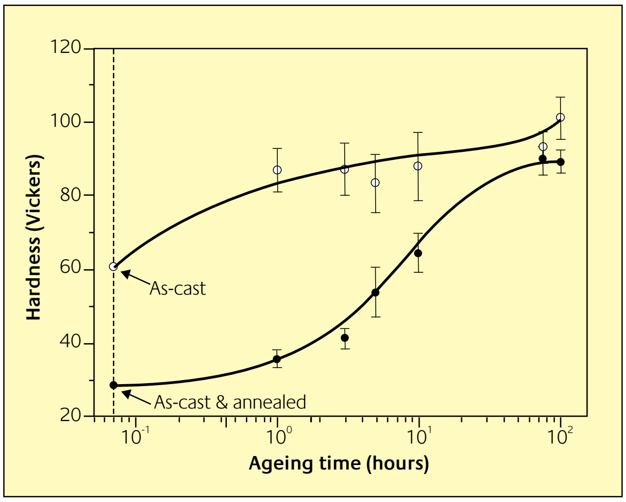

Figure 8

The influence of ageing at 300°C on the hardness of the alloy in the as-cast state, and in the annealed condition after casting (with 95% confidence interval)

casting results in a decrease in hardness to approximately 29 HV5. Subsequent ageing at 300°C raises the hardness (as shown in Figure 8), but the hardening process is retarded as a result of the lack of cold work prior to ageing. Ten hours at temperature increased the hardness only to the initial as-cast value. Although the hardness can be increased to almost 90 HV5, the time required to reach this peak hardness makes the

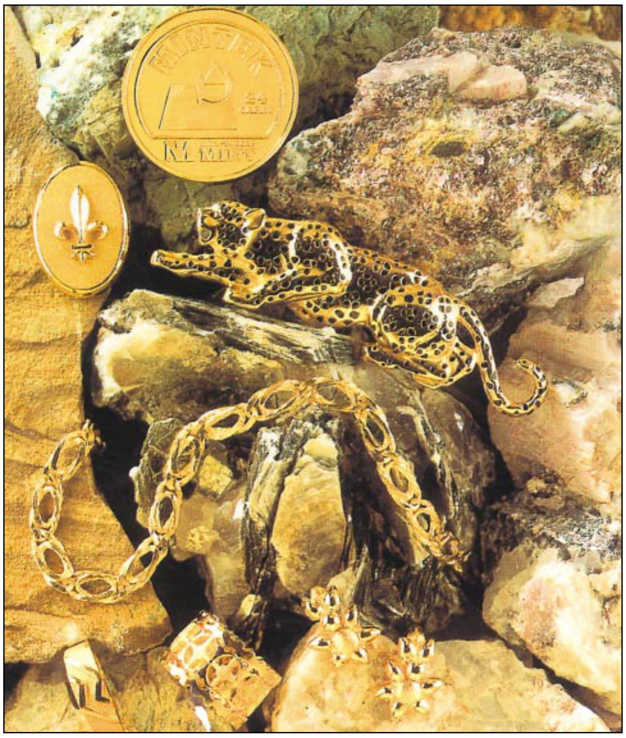

Figure 9

Examples of jewellery pieces (design: David Bolam, South Africa) and a one ounce medallion (design: Independent Mint, South Africa) produced using the 995 alloy

heat treatment impractical, and a fast cooling rate after solidification is therefore recommended.

Examples of jewellery cast under the conditions described above are shown in Figure 9. Even very intricate jewellery pieces can be produced without any difficulty. Very good surface finishes were obtained, and polishing presented no problems.

Industrial Scale Casting Trials

During the industrial casting trials, two kilograms of 995 alloy granules was remelted at Rand Refinery in South Africa under an inert atmosphere in graphite moulds generally used for the production of pure gold kilobars. An induction furnace with a peak temperature of 1200°C was used. Except for limited signs of shrinkage porosity in the centre of the castings, the bars appeared similar to the 24 carat kilobars routinely produced at Rand Refinery, with smooth, clean surfaces after casting. The only visible difference was that the equiaxed grains in the 995 casting had a typical diameter of about 1mm, compared to 5mm in the case of the standard 24 carat kilobars.

Industrial Scale Processing Trials

In order to characterise the alloy's behaviour during processing on a larger scale, granulation, wire-drawing and rolling trials were performed at Rand Refinery in South Africa. To obtain enough material to perform the required tests, twelve kilograms of the alloy were melted under an inert atmosphere in a graphite crucible in an induction furnace. The molten alloy was subsequently granulated by pouring the liquid metal through small holes in the bottom of the crucible, directly into cold water. The granules were homogeneous, lumpy in appearance rather than flaky, deep yellow in colour, and free of oxidation. The granules were then remelted and cast to produce the kilobars described in the 'Industrial Scale Casting Trials' section above. Remelting was very successful. Alloying element losses were negligible, and the alloy could be rehardened to the levels presented earlier in Table 3.

After remelting and casting a small piece of a kilobar was sectioned off (initial cross section 9mm x 9mm) and manually drawn through a wire-drawing mill to a final cross-section of 1mm x 1mm. Two intermediate annealing steps (the first at a cross-section of 4mm x 4mm and the second at 1.7mm x 1.7mm) were used. The wire displayed no surface defects or cracks.

In order to evaluate the behaviour of the alloy during rolling, the kilobars, with initial dimensions of 110mm x 50mm x 9mm, were rolled down to a thickness of 1mm using a combination of cold work and intermediate annealing. All annealing at Rand Refinery was performed at 730°C under an inert atmosphere to prevent oxidation. The amount of deformation during the final rolling step was varied from 20 per cent to 80 per cent. No problems were encountered during the rolling process. The conclusion can be drawn that the industrial scale processing trials were successful and that the 995 alloy is amenable to granulation, casting, remelting, wire drawing, forming and rolling.

Production of Coins and Medallions

The inherent softness of pure gold often creates problems during coin striking operations due to poor die-filling characteristics and the formation of shuts. The hardness of the 995 alloy after solution annealing and cold rolling (ranging from approximately 85 HV5 after 50 per cent rolling reduction, to 115 HV5 after 80 per cent rolling reduction) is well suited to the production of coins and medallions. In addition, the coins or medallions can be age-hardened at 300°C after striking, making them more scratch-resistant and less susceptible to damage.

Coining trials were carried out with the assistance of the Independent Mint in South Africa. Samples of the alloy were annealed and cold rolled to a thickness of 1.8mm (corresponding to a hardness of approximately 90 HV5). Subsequent to rolling, 32mm diameter blanks were struck and rimmed. The blanks were polished to a mirror finish and medallions were struck using loads of up to 140 tonnes. In order to increase definition, proof-quality blanks were struck up to three times. As a result of the excellent formability of the alloy, no annealing steps were required between the rolling, blanking and striking operations.

The high gold content of the 995 alloy allows coins and medallions to be marked as 24 carat gold in most countries. An example of such a medallion is shown in Figure 9.

Conclusions

Mintek has developed a hard Au-Sb-Co ternary alloy with 995 fineness that has some notable advantages:

1 The alloy can be hardened to a value in excess of 130 HV5 using a combination of cold work and a low-temperature ageing heat treatment. This hardness is comparable with the hardness of cold-worked 22 carat yellow gold, and almost double the maximum hardness that can be achieved in pure gold. The ultimate tensile strength of the 995 alloy in the cold-worked and aged condition is twice that of cold-worked pure gold.
2 The high gold content of the alloy (99.5 per cent) facilitates marking as 24 carat gold (or *Chuk Kam*) in many countries, including South Africa, Europe, China, Taiwan, Hong Kong, and South Korea.
3 The 995 alloy is highly formable, as evidenced by rolling, deep drawing and cupping tests.
4 The colour of the alloy is virtually identical to that of pure gold.
5 Casting trials on both the laboratory and industrial scales were successful. The alloy is also amenable to granulation, remelting, wire drawing, forming and rolling.
6 The increased hardness and excellent formability of the alloy make it suitable for the production of 24 carat gold coins and medallions.

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